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Extensive studies have been made on poled Nonlinear Optical (NLO) guest-host systems. The limited solubility of the NLO species in a host matrix and the thermal relaxation of the induced nonlinear optical activity of the poled polymeric films are major disadvantages. Side chain polymers have attracted attention since a large number of NLO molecules may be covalently attached to the polymer chain and the problem of phase segregation of the NLO component is alleviated. In this article, we present the second and third order NLO properties of a new class of guest-host system which possess excellent doping features and photoreactive characteristics.

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Nonlinear Optical Properties of New Dye Doped
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by

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NONLINEAR OPTICAL PROPERTIES OF NEW DYE DOPED PHOTOCROSSLINKABLE POLYMERS

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INTRODUCTION

Polymeric materials are playing an increasingly important role in electronic and photonic applications[1-4]. This includes application in active devices utilizing optical effects attributable to the nonlinear polarization of the medium. A number of applications such as frequency mixing, second harmonic generation, optical bistability, optical parametric amplification and oscillation, electrooptic and all optical switching and modulation etc. have been proposed.

There is a separation of charges in a nonlinear optical (NLO) medium under the application of an electric field. For weak electric fields, the applied electric vector, E, induces a polarization, P, in the material which is linearly dependent on the electric field. $P_{linear} = \chi^{(1)} E$, where $\chi^{(1)}$ is the susceptibility tensor. The net polarization in the medium under the influence of several fields is a linear superposition of the effects of the same fields acting independently. At high intensities the optical fields can interact with each other through the higher order terms in the polarization vector. P can now be expanded as $\chi^{(1)} E + \chi^{(2)} E^* E + \chi^{(3)} E^* E^* E + ...$ The nonlinear susceptibilities, $\chi^{(2)}$, $\chi^{(3)}$, etc., of the medium represent the magnitudes of the higher order interactions with the applied fields. These properties are dictated by features at the molecular level; including electronic and molecular structure and the nature of the overall molecular packing.

Extensive studies have been made on poled NLO guest-host systems[5-7]. The limited solubility of the NLO species in a host matrix and the thermal relaxation of the induced nonlinear optical activity of the poled polymeric films are major disadvantages. Side chain polymers have attracted attention since a large number of NLO molecules may be covalently attached to the polymer chain and the problem of phase segregation of the NLO component is alleviated[8]. In this article, we present the second and third order NLO properties of a new class of guest-host system which possess excellent doping features and photoreactive characteristics.

MATERIALS REQUIREMENTS

For second order NLO properties, a noncentrosymmetric organization is essential. This is not necessary for third order NLO properties. In addition to large optical nonlinearity of the material, the ease of processing is also important from the standpoint of device fabrication. Strong electron donor and acceptor groups in a π-conjugated structure has been used to promote intramolecular charge transfer, which is important for large second order hyperpolarizability. These molecular systems can be incorporated into a host polymer for effective processing. Noncentrosymmetric alignment of the NLO species in the guest-host systems can be introduced by electric field induced poling[9]. Third order nonlinear susceptibility of guest-host systems incorporating the conjugated molecules is also of current interest because of the possibility of making low loss guided wave devices from these materials. The origin of large third order nonlinearity lies in the extended π-conjugation effect[3].

Design of nonlinear optical polymers based on the guest-host approach calls for molecular structures that, in addition to large molecular hyperpolarizability, will also be compatible with the host polymer. Any phase segregation of the NLO species will adversely effect the optical quality of the polymeric film. Transparency at the wavelength of operation is also desired. For second order application the NLO species are poled, resulting in a net polarization for the medium. In the poling process, a noncentrosymmetric organization is produced. In addition, the alignment yields the largest second order nonlinear coefficient in the direction of the poling field. Largest component of the molecular hyperpolarizability is usually along the molecular axis.

MATERIALS AND METHODS

Within the scheme of a guest-host system, suitable combinations of guest and host molecules have led to higher NLO concentrations and more stable NLO response. Copolymers such as styrene acrylonitrile (SAN) have been found to be better hosts compared to conventional glassy homopolymers such as polystyrene (PS) or polymethyl methacrylate (PMMA)[10]. Higher concentrations of polar dyes could be incorporated prior to phase segregation and the poled organization possessed greater temporal and thermal stability (Figure 1).

In our laboratory, a new route to achieve a stable crosslinked NLO polymer system by photochemical reaction has been developed. This class of guest-host systems has been designed from first principal to be compatible leading to extremely high levels of dye loading without phase segregation. Large third and second order nonlinear susceptibilities have been measured for the guest-host unpoled and poled crosslinked systems, respectively. Approaches to fabrication of nonlinear optical devices have also been developed which takes advantage of the excellent processability and photocrosslinking behavior of the polymers[11].

A donor-acceptor substituted azo dye was selected as the basic NLO species. These dyes have been reported to possess some of the largest molecular hyperpolarizabilities[12]. The NLO dye was functionalized at two sites using photoreactive chromophores.

Cinnamoyl (C_6H_5-CH=CH-CO-) and styryl-acryloyl (C_6H_5-CH=CH-CH=CH-CO-) groups were selected as the desired photoreactive groups. The phenyl rings may be further suitably derivatized to modify the spectral features, photosensitivity and photoselectivity. An example of this type of NLO molecules is 2,2'-bis(cinnamoyloxy) -4-diethylamino-4'-nitroazobenzene (CNNB-R) (Figure 2). Clearly, many other variations in structure may be introduced to carry out spectral tuning, optimization of the NLO properties, conformational features and the overall stability of the molecule[13].
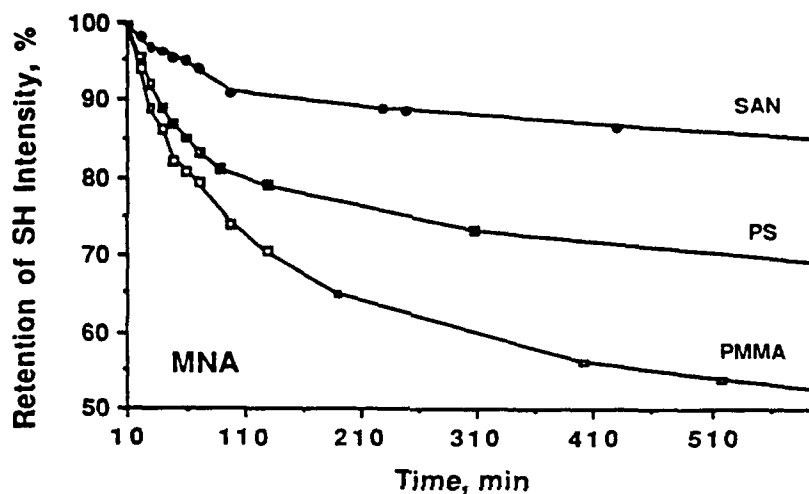
Figure 1.   Temporal behavior of 2-methyl-4-nitroaniline (MNA) molecules in homo- and copolymers.
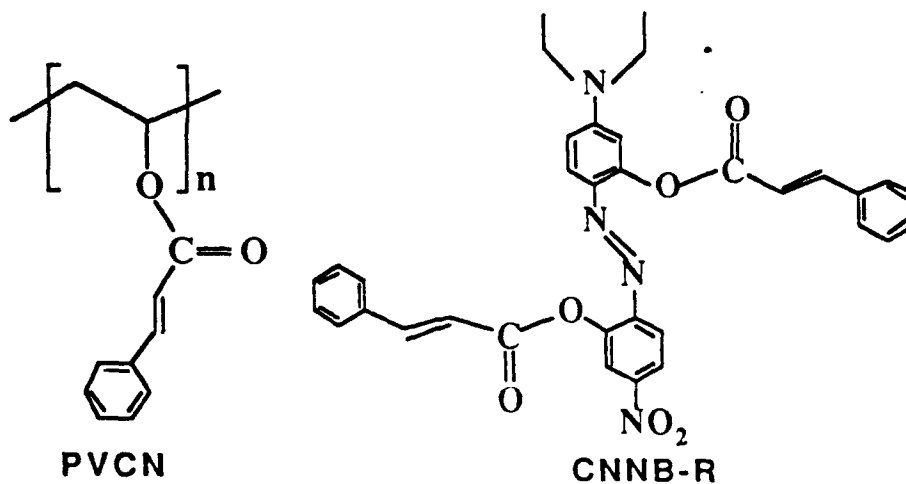

PVCN   **CNNB-R**

Figure 2.   Structures of new photocrosslinkable guest-host system.

The desired host polymer should contain a large number of the same photoreactive group. It should have excellent film forming properties and preferably be glassy with a moderately high T_g to facilitate processing at not too high a temperature. Its overall compatibility with the guests should be helped by the presence of similar functional groups, but is not assured.

The simplest and commercially available polymer polyvinylcinnamate (PVCN) was chosen as a candidate host polymer (Figure 2). This polymer is synthesized by esterification of polyvinyl alcohol with cinnamoyl chloride[14]. A PVCN with a large degree of derivatization (>70%) is appropriate for effective solid state photoreaction process. Compatibility of this polymer among other parameters will be dominated by the interaction of the photoreactive groups with similar groups in the guest. The polymer backbone is relatively flexible and the guest dye has an articulated structure.

For third order nonlinear application, however, it is the concentration of the NLO dye that is of paramount importance, not the orientational aspects. The third order response is typically dependent on the extent and nature of electronic conjugation. Polydiacetylene, for example, shows very high $\chi^{(3)}$ because of the delocalized electronic structure along the π-conjugated polymer chains[15]. The large dye molecules posses quite reasonable molecular hyperpolarizability. A high concentration of these dyes without a concomittant deterioration of linear optical properties can lead to useful bulk third order NLO coefficients.

Processing

Thin films may be prepared by spin coating from a solution of PVCN and CNNB-R in toluene/chlorobenzene (1:3 v/v) mixture. 100 parts of PVCN and 0, 10, 20, 30, 40, 50 parts of CNNB-R by weight were made into a saturated solution. The solutions were filtered through a 1 μm membrane filter and then spun on glass or quartz plates at 3000 rpm, resulting in film of thickness from 0.5 - 1 μm as measured by ellipsometry. Films were dried at 60° - 70° C in a vacuum oven overnight.

Linear Spectroscopy

Thin films spin coated on quartz plates are used for UV-visible spectroscopy. The absorbance from the films at the characteristic wavelength at which the dye absorbs scales linearly with dye concentration, establishing a homogeneous distribution. UV-visible spectrum further establishes the desired wavelength for most effective photocrosslinking[16]. A small concentration (<1%) of conventional sensitizer such as coumarin or thiazoline dye can also be used to effectively shift the crosslinking radiation to longer wavelengths. Practically, any wavelength light from UV to mid visible is adequate for crosslinking in conjunction with an appropriate sensitizer.

The optical constant such as refractive index, and the thickness of a film are determined by ellipsometry. For polymer thin films the reflection ellipsometry technique is commonly used[17]. This technique is especially useful in the wavelength regions where the materials are strongly absorbing so that the transmission measurements are precluded.

The thickness and the refractive index of the polymer film can also be measured more precisely by optical waveguiding techniques. The planar wave guide technique in which the light is confined in one direction only is widely used for this purpose[18]. Table 1 summarizes some of the linear optical properties of photoreactive polymer films.

Poling and Photocrosslinking

Corona poling technique in the wire to plane geometry as well as parallel electrode poling techniques have been used to pole these classes of polymers in film form. Poling is carried out prior to crosslinking to align the NLO units and possibly poise the photoreactive groups for photo-induced solid state reaction.

The poling temperature was set about 70° C, which is 10° C below T_g of the uncrosslinked guest-host system. UV irradiation from a mercury lamp at 254 nm, producing an intensity of 2 mW/cm^2 on the film surface was used for crosslinking. The optimum exposure time was established from the UV-visible spectra of the doped polymer films.

Photocrosslinking may be carried out by exposure to UV radiation. Crosslinks are formed by 2 + 2 photodimerization between an excited cinnamoyl group with another in the ground state. It is expected that a sufficient number of these pairs will belong to the same or different molecules to form a crosslinked network. The intermolecular crosslinking reaction between the photosensitive chromophores is represented in Figure 3.
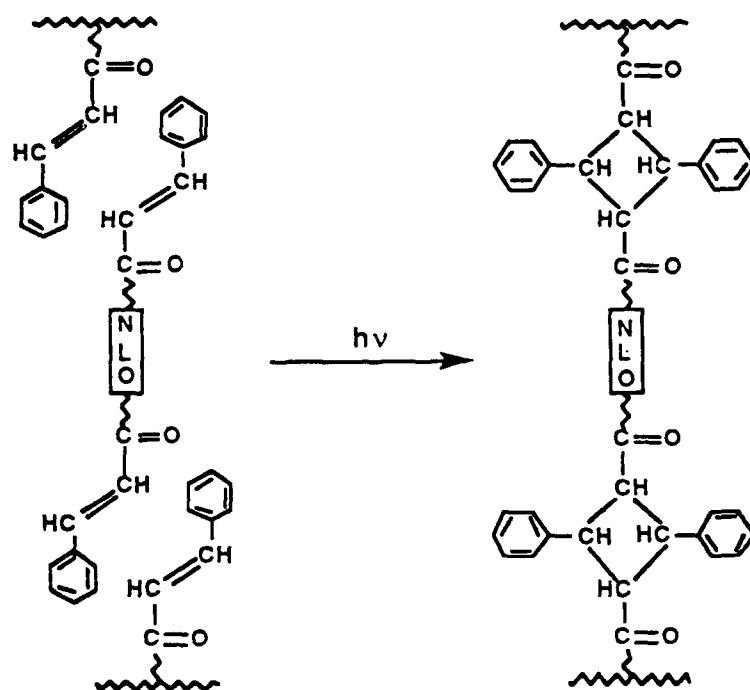
Figure 3. One of the photocrosslinking mechanisms in guest-host system.

Second Order Properties

The second order nonlinear susceptibility of the polymer has been measured by comparing the second harmonic intensity from the polymer films with that of Y-cut crystal quartz. The stability of the second harmonic signal with time after poling and crosslinking have been observed with PVCN doped with 20 % by weight of CNNB-R (Figure 4). The results clearly indicate that the poled and crosslinked polymer is quite stable in its second harmonic signal, while the polymer film which has not been crosslinked during the poling process shows substantial decay in SHG signal with time. The same UV cured polymer shows no decay in SHG intensity upon heating at 80°-85°C for long periods of time. Linear electrooptic coefficient of doped poled and crosslinked films have been measured. Second order coefficient, d_{33}, of up to 30 pm/V have been measured for these guest-host systems. The results of some of these measurements are summarized in Table 1.
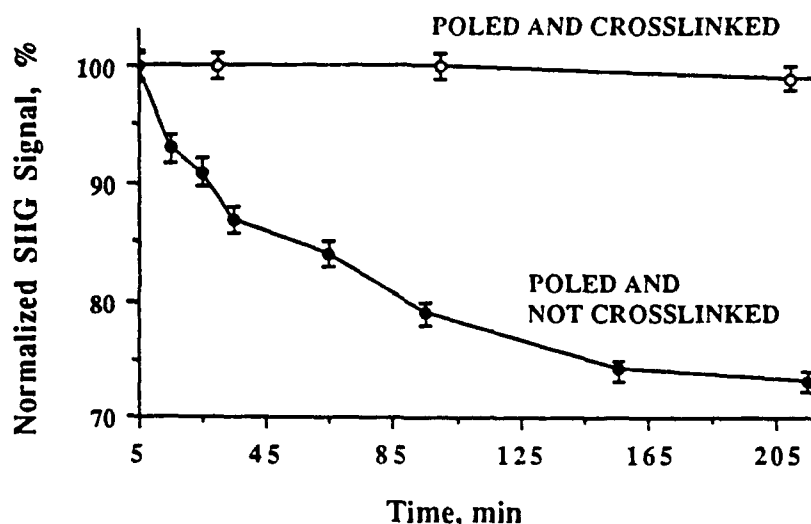

Figure 4. Stable NLO behavior of photocrosslinkable guest-host system.

Table 1. Properties of photocrosslinkable guest-host system.

PVCN/CNNB-R (%)	(10%)	(20%)
Thickness (μm)	0.5	0.5
Abs. max (nm)	520	520
T_g (°C)[a]	84.3	81.0
Refractive index		
λ (μm)		
0.532	1.632	1.634
0.632	1.677	1.685
1.000	1.613	1.625
d_{33} (pm/V)		
1.063μm	11.5	21.5
1.540μm	3.7	5.1

[a]Obtained from DSC (DuPont 2910 differential scanning calorimeter), 10°C/min (midpoint). T_g of PVCN is 88.1°C

Thermal Properties

Thermal analysis techniques were used to investigate thermal stability and relaxation behavior in the crosslinked and uncrosslinked samples. To measure T_g and ΔC_p at T_g upon photocrosslinking, a DSC set up has been used. DSC curves of PVCN and PVCN/20 % CNNB-R after different periods of crosslinking radiation are shown in Figure 5. As seen in Figure 6, UV-radiation does not lead to a large increase in T_g. UV exposure results in to extensive crosslinking and increase in the beam penetration depth. In the thin films unreacted sample material is decreased. As the material is completely crosslinked the medium loses the glass rubber transition.
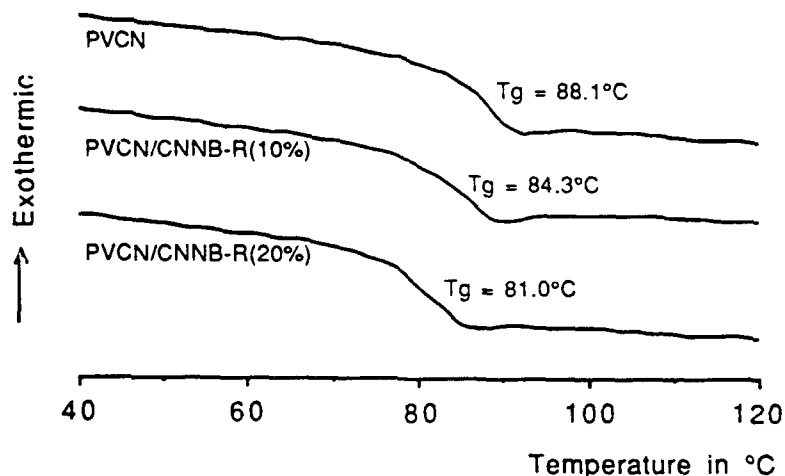
Figure 5. DSC curves of PVCN and PVCN doped with CNNB-R.
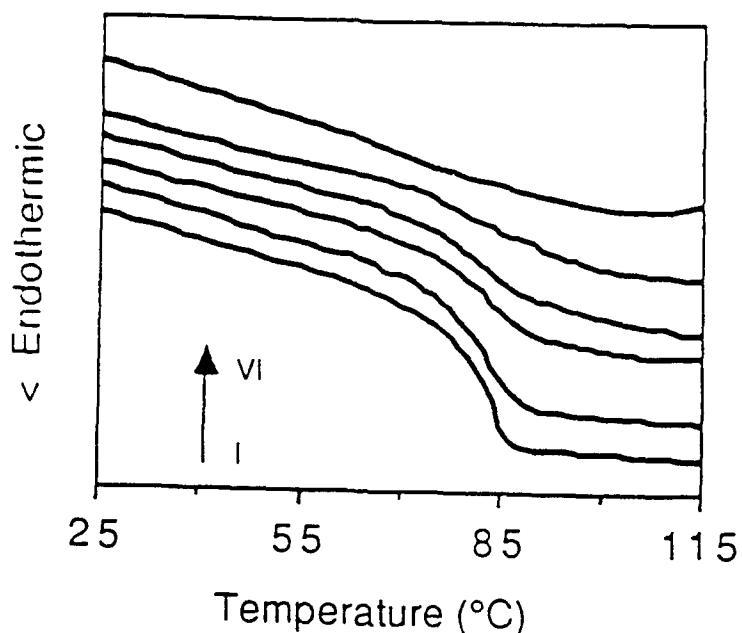
Figure 6. DSC curves of PVCN films doped with 10% CNNB-R. Crosslinking was performed by UV radiation at wavelength 254 nm; I=0, II=1, III=3, IV=5, V=10, VI=30 min respectively.

Third-order nonlinear optical properties

Third-order nonlinear optical properties (namely, quadratic electrooptic coefficient) of this polymeric system at different dye concentrations have been measured using a modified Michelson interferometer[19] at 633nm. For this measurement, the polymer film was spin-coated from the filtered solution on an indium-tin-oxide (ITO) coated glass plate where the ITO layer was used as an electrode. A gold layer of 500Å thickness was thermally evaporated onto the polymer film to form the second electrode. The experimental set-up of this modified Michelson interferometer is schematically shown in (Figure 7).

A HeNe laser beam is split into a sample beam and a reference beam. The sample beam propagates via the ITO coated glass and the polymer film, and is then reflected back by the gold electrode. An AC-modulating field (about 5 kHz) was applied across the polymer film. A detector was employed to measure the modulations at two half-intensity points of a selected interference fringe at 2ω, noted as $I_{2\omega}^{+}$ and $I_{2\omega}^{-}$. Then the quadratic electrooptic (E-O) coefficient, S_{1133}, as a measure of the third order optical nonlinearity is given by:

$$S_{1133} = (1/\pi\, n^3)\, [(I_{2\omega}^{+} - I_{2\omega}^{-})/(I_{max} - I_{min})]\, (\lambda\, d/\, V_m^2)$$

where n is the refractive index, λ is the laser wavelength, d is the thickness of the film, V_m is the modulating voltage, and I_{max} and I_{min} are the maximum and minimum intensities of the selected fringe, respectively.

The measured quadratic E-O coefficient as a function of dye concentration is shown in Figure 8. An approximately linear relationship exists between them, which indicates no aggregation in this dye doped polymer system. The quadratic E-O coefficients in this system are large compared with those of our former systems[20] based on azomethine dyes and those reported recently by Kuzyk et al[21] at the same dye concentrations.
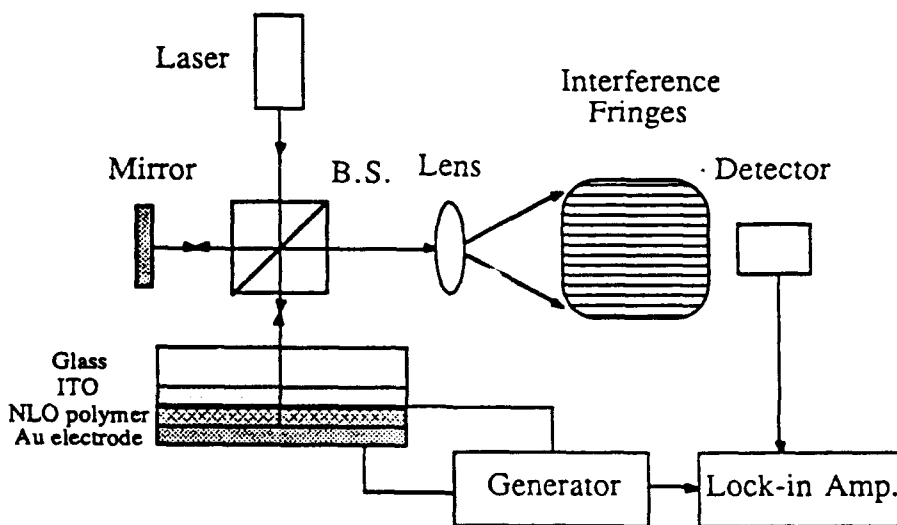

Figure 7.   Experimental set-up for the measurement of quadratic electrooptic coefficient.
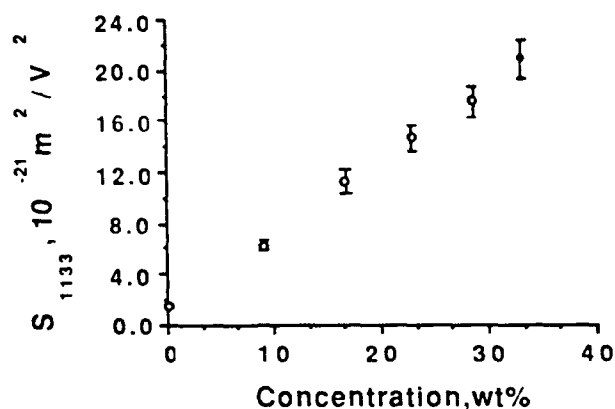
Figure 8. Effect of quadratic E-O coefficient with
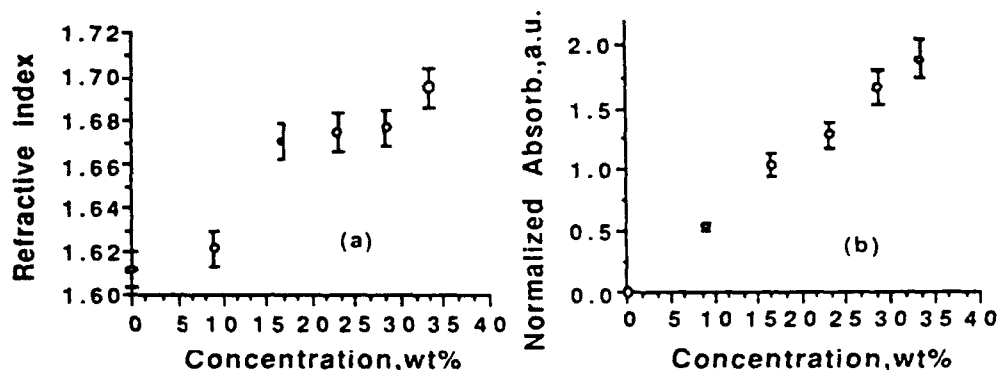the concentration on the NLO dye.

Figure 9. Linear optical properties of dye doped polymer film. (a) Change in
refractive index with increasing dye concentration. (b) Change in
normalized absorbance with increasing dye concentration.

In addition to the quadratic E-O coefficient measurement, the linear optical properties of those films were measured using an ellipsometer and a UV-visible spectrophotometer. The measured refractive index (at 633 nm) and normalized peak absorbance of those films are also approximately linear with the dye concentration (up to 33 wt%), which are shown in Figures 9a and 9b, respectively. These results also show that no phase segregation occurred in this dye doped polymer system for dye concentration up to 33 wt%.

ACKNOWLEDGEMENT

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